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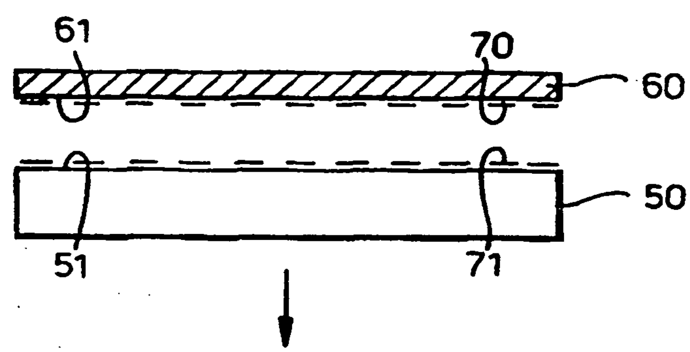
(54) Title: GLASS-CERAMIC COATINGS AND SEALING ARRANGEMENTS AND THEIR USE IN FUEL-CELLS

(57) Abstract

To provide effective seals between the separator plates of fuel cells, particularly planar solid oxide fuel cells (SOFC's), a method of applying a glass-ceramic coating to such a separator plate (50) comprises providing a laminar body incorporating a glass powder, e.g., a tape-cast sheet (60), forming a bond between the laminar body (60) and the separator plate to form an assembly comprising the separator plate and the laminar body and heat treating the assembly to convert the glass-powder to a glass-ceramic.



GLASS–CERAMIC COATINGS AND SEALING ARRANGEMENTS AND THEIR USE IN FUEL–CELLS

This invention is concerned with a method of forming a glass-ceramic coating on a substrate and to coatings produced thereby, such coatings having particular but not exclusive utility in the provision of sealing arrangements between non-porous separator plates of fuel cells, particularly planar solid oxide fuel cells (SOFC's), and includes methods of producing such sealing arrangements.

The present invention has particular advantages when used to produce seals between separator plates which are metal or metallic: in the context of this specification the terms 'metal' and 'metallic' are to be interpreted as meaning not just plates made of metals and exclusively metal alloys, but also of oxide dispersion strengthened metal alloys which include a relatively small percentage of an oxide or oxides incorporated therein.

A planar SOFC comprises a stack of vertically spaced impermeable separator plates. These separator plates separate the reactant gases and also provide electrical connection between adjacent cells. In the space between each adjacent pair of plates is held one or more cells each comprising a solid electrolyte having an anode and a cathode. Clearly, in view of their separator function, the separator plates must not be porous as they comprise part of a gas-tight assembly. The reactant gases comprise a fuel gas (e.g. hydrogen or carbon monoxide) and an oxidant (e.g. oxygen or air) and are respectively supplied to the anode and the cathode by suitable ducts which may, for example, be provided by channels in the upper and lower surfaces of the adjacent separator plates. As is known, the reactions at the electrode cause a voltage. Connection between the electrodes and adjacent separator plates can be either by direct contact or via an electrically conducting interlayer. For example a current collector (e.g. a nickel grid) may be provided adjacent the anode and a conductive porous sheet may be provided adjacent the cathode or the cathode may contact a conductive coating on the separator plate.

SOFC's usually operates at temperatures in the range 750°C- 1000°C, though it is envisaged that they could operate at lower temperatures, possibly as low as 650°C. In a planar SOFC

Another aim of the invention is to provide an effective high-performance non-porous glass-ceramic seal between adjacent non-porous separator plates of planar SOFC's.

A further aim is to produce such a seal capable of electrically insulating adjacent biploar plates from each other and preventing electronic leakage therebetween.

Another aim is to provide such a seal which accommodates change in dimension of the stack during its manufacture.

A further aim of the invention is to provide a method of applying a glass-ceramic coating to a separator plate for a solid oxide fuel cell, so providing a base layer for at least one further layer required to complete a seal between confronting surfaces of adjacent separator plates.

It is to be understood that a glass-ceramic is an inorganic, polycrystalline material formed by the controlled crystallisation of a glass; a glass on the other hand is an inorganic material formed by fusion but wherein the material has cooled to a rigid condition without crystallising.

According to a first aspect of the invention, a method of providing a glass-ceramic coating having improved bonding to a substrate comprises the steps of: depositing a first bonding layer of glass powder mixed with a binder directly onto the substrate (preferably using a screen printing or spraying process); adhering a laminar body comprising glass powder mixed with a binder to the first layer to form a second layer which is substantially thicker than the first layer, the glass powder in both layers being of a composition such as to form a glass-ceramic on heat treatment; and heat treating the resultant green coating on the substrate to drive off the binder and convert the glass powder layers to glass-ceramic layers.

According to a second aspect of the invention, in a fuel cell, a high-performance seal between confronting faces of adjacent non-porous separator plates comprises at least one glass-ceramic layer on at least one of the confronting faces and at least one glass seal layer interposed between the at least one glass-ceramic layer and the other separator plate.

whereby when the laminar body and the substrate are brought into contact an adhesive bond is formed between the laminar body and the substrate; during heat treating of the assembly the binder is burned out before formation of the glass-ceramic.

Alternatively, prior to bringing the laminar body and the substrate into contact, a thin bonding layer incorporating a glass powder of composition such as to form a glass-ceramic upon heat treatment is applied to the substrate to provide an bonding layer to which the laminar body is then bonded. In this embodiment the bonding layer may be applied by spraying or screen-printing, the laminar body then being applied while both layers are in the green condition. During heat treatment, the glass-powder in the bonding layer becomes a glass-ceramic layer and forms a bond between the substrate and the layer produced by the laminar body. The glass-powder of the bonding layer may have a different composition to that of the glass powder incorporated in the laminar body, the glass-powder compositions of the laminar body being optimised to reduce thermal stress between the substrate and the seal on formation of the glass-ceramic and the glass-powder compositions of the bonding layer being optimised so as to flow upon melting and wet the substrate before crystallisation occurs.

It is particularly envisaged that the above method is utilised to form a seal between two adjacent separator plates of a fuel cell, the method involving the additional step that a layer of glass is applied to the glass-ceramic or that a layer of glass and glass-ceramic is applied to said glass-ceramic.

The or each separator plate may be formed of a metal or a metal alloy, e.g., a ferritic stainless steel or a high chrome alloy; such a chrome alloy may have a composition including Cr, Fe and Y_2O_3, for example 95%Cr, 5%Fe and 1% Y_2O_3. Further, the or each plate may be coated with an alloy or an oxide e.g. with an oxide of formula $La_x Sr_{1-x} CrO_3$

The laminar body mentioned above comprises a mixture of glass powder and a binder in the form of a tape or sheet of material (produced, e.g., by tape-casting or calendering). The

the overlying glass-ceramic layer.

In providing a seal for an SOFC, a glass-ceramic coating is formed as indicated above (single or duplex layers), and a sealing glass layer is then provided so that the seal is effectively a double layer comprising the glass-ceramic coating and a sealing glass layer. The combination of glass and glass-ceramic layers provide a gas-tight seal to separate and contain the reactant gases and electrically isolate adjacent bipolar plates. The main function of the glass-ceramic layer is to provide high temperature electrical insulation between the bipolar plates although it also must be gas-tight to contain the reactant gases. Conversely, the glass seal layer provides some measure of electrical insulation although not having as high electrical resistance as the glass-ceramic at the operating temperature. By using a glass rather than a glass-ceramic for the actual sealing stage of stack assembly the seal can continue to deform after sealing (under weight of the stack) to ensure the cell components remain in electrical contact through the stack. A glass is able to deform by viscous flow whereas a glass-ceramic, once crystallised, does not deform appreciably. The glass seal can be applied as a sheet or as a powder glass/binder mixture.

By using a glass powder composition that gives a glass seal layer of high viscosity during the heat-treatment, flow of the glass is minimised ensuring that coating thickness can be closely controlled and that the coating will closely conform to the stamped out pattern of the laminar body.

Compositions and heat-treatments of the glass-ceramic layers are selected so that their thermal expansions are closely matched to that of the separator plates to minimise stresses during thermal cycling. This may be achieved, for example, by producing two different glass powders in the $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ system which have widely different coefficients of thermal expansion. The two glass powders may then be mixed together in the appropriate ratio to give a glass-ceramic coating composition of the required thermal expansion. The coefficients of thermal expansion can for example be varied in the range $8.5\text{-}11.5\times10^{-6}\,K^{-1}$, 25-1000°C.

an anode layer 18 on the other (lower) surface. As shown in Figure 1 the layered assembly 15 takes the form of a two-by-two electrode array but other arrangements are possible, e.g. the layered assembly may be in the form of a single electrode or it could be in 3 x 3 or 2 x 4 arrays, for example. The porous layer(s) or sheet(s) 13 will be dimensioned to correspond with the array. As shown in Figure 4(a), a current collector 19, e.g. in the form of a nickel grid, is affixed below the anode 18, on top of anode-contacting surface 14 of plate 11.

As seen in Figures 1 and 4(a), each bipolar or separator plate 11 is formed with a gas flow channel arrangement 20, 21 formed respectively on its upper surface and its lower surface, through which channel arrangements flow the fuel gas and the oxidant gas respectively. The channel arrangements 20, 21 take the form of parallel channels 22 in the upper surface and parallel channels 23 in the lower surface, the channels in the respective surfaces being oriented transversely relatively to each other.

The gas flow channels 22 in the upper surface distribute a fuel gas (e.g. hydrogen, carbon monoxide, methane, or natural gas) entirely and evenly over the adjacent anode 18 and the gas flow channels 23 in the lower surface distribute the oxidant gas (e.g. oxygen, air) entirely and evenly on the adjacent cathode 17.

The separator plates are formed with apertures 24, 25, 26 and 27 therethrough, so that when the stack of cells is assembled they form, respectively, passages for fuel gas to reach channels 22, passages for oxidant gas to reach channels 23, passages for the exhaust of spent and unused fuel gas and passages for the exhaust of spent and unused oxidant gas.

Reference 29 indicates a sealing arrangement between adjacent separator plates and comprises a layer 30 of glass-ceramic insulation and a sealing layer 40 of glass or of glass and glass ceramic.

The glass-ceramic layer 30 is deposited onto the cathode-contacting face 12 of the separator plate 11 prior to assembly of the SOFC stack and the glass (or glass and glass-ceramic) layer 40 bonds together adjacent separator plates and seals the electrolyte assembly to the

by a glass-ceramic layer 30 formed as described with reference to Figure 2 or Figure 3 and a glass layer 40, with the glass layer being of sufficient area to bind and seal to the solid electrolyte 16, as shown at interface 42.

In Figure 4(b) is shown an arrangement which in addition to the layers 30, 40 of Figure 4a comprises a screen-printed glass-ceramic bond layer 45 formed on the cathode face 12 of the separator plate.

In Figure 4(c) screen-printed glass-ceramic bond layers 45, 46 are provided respectively on both cathode- and anode-contacting faces of the separator plates, in addition to the layers 30, 40. However, such a layer 46 may be of more value as a protective layer than as a bonding layer, by forming a barrier between the seal layer 40 and the separator plate, to obviate the possibility of unwanted reactions between the seal layer 40 and the separator plate.

Figure 4(d) shows a modification of the embodiment of Figure 4(c) but in this embodiment an additional screen-printed glass-ceramic layer 41 is provided between sealing glass layer 40 and glass-ceramic bond layer 46.

It will be seen from the above that by suitable selection of the number and composition of the glass layers in the inter-plate sealing arrangement 29^1, it is possible to tailor their properties to simultaneously achieve, during manufacture and service of the SOFC stack, good bonding to the plates 11; good matching of thermal expansion coefficients; good sealing and insulation between plates 11 and between adjacent cells in each planar array of cells; and good electrical contacts within the cells.

The following Table gives exemplary compositions of glasses and glass-ceramics useful for putting the present invention into effect.

CLAIMS

1. A method of providing a glass-ceramic coating having improved bonding to a substrate comprises the steps of: depositing a first, bonding, layer of glass powder mixed with a binder directly onto the substrate; adhering a laminar body comprising glass powder mixed with a binder to the first layer to form a second layer which is substantially thicker than the first layer, the glass powder in both layers being of a composition such as to form a glass-ceramic on heat treatment; and heat treating the resultant green coating on the substrate to drive off the binder and convert the glass powder layers to glass-ceramic layers.

2. A method according to claim 1 in which the first layer is applied by one of a screen printing and a spraying process.

3. A method according to claim 1 or claim 2 in which the first layer is not more than about 50μm in thickness.

4. A method according to any preceding claim in which the second layer is between about 100μm and 3mm in thickness.

5. A glass-ceramic coating when made by the method of any one of claims 1 to 4.

6. A high-performance seal between confronting faces of adjacent separator plates in a planar solid oxide fuel cell stack comprising at least one glass-ceramic layer on at least one of the confronting faces and at least one glass seal layer interposed between the at least one glass-ceramic layer and the other separator plate.

7. A high-performance seal according to claim 6, in which the at least one glass-ceramic layer is a duplex layer, comprising a first glass-ceramic layer for bonding the seal to the separator plate and a second glass-ceramic layer superimposed on the first glass-ceramic layer, the glass seal layer being interposed between the second glass-ceramic layer and the adjacent separator plate, the second glass-ceramic layer being substantially thicker than the first glass-ceramic layer.

15. A method according to Claim 14, wherein the laminar body incorporates a binder and prior to bringing the laminar body and the substrate into contact a solvent is applied to the substrate and/or to the laminar body, whereby when the laminar body and the substrate are brought into contact an adhesive bond is formed between the laminar body and the substrate.

16. A method according to Claim 14 wherein prior to bringing the laminar body and the substrate into contact a bonding layer incorporating a glass powder is applied to the substrate to provide an adhesion layer to which the laminar body is then bonded.

17. A method according to Claim 16, wherein said bonding layer is applied by spraying or screen-printing.

18. A method according to Claims 16 or claim 17, wherein the glass-powder of the bonding layer has a different composition to that of the glass-powder incorporated in the laminar body.

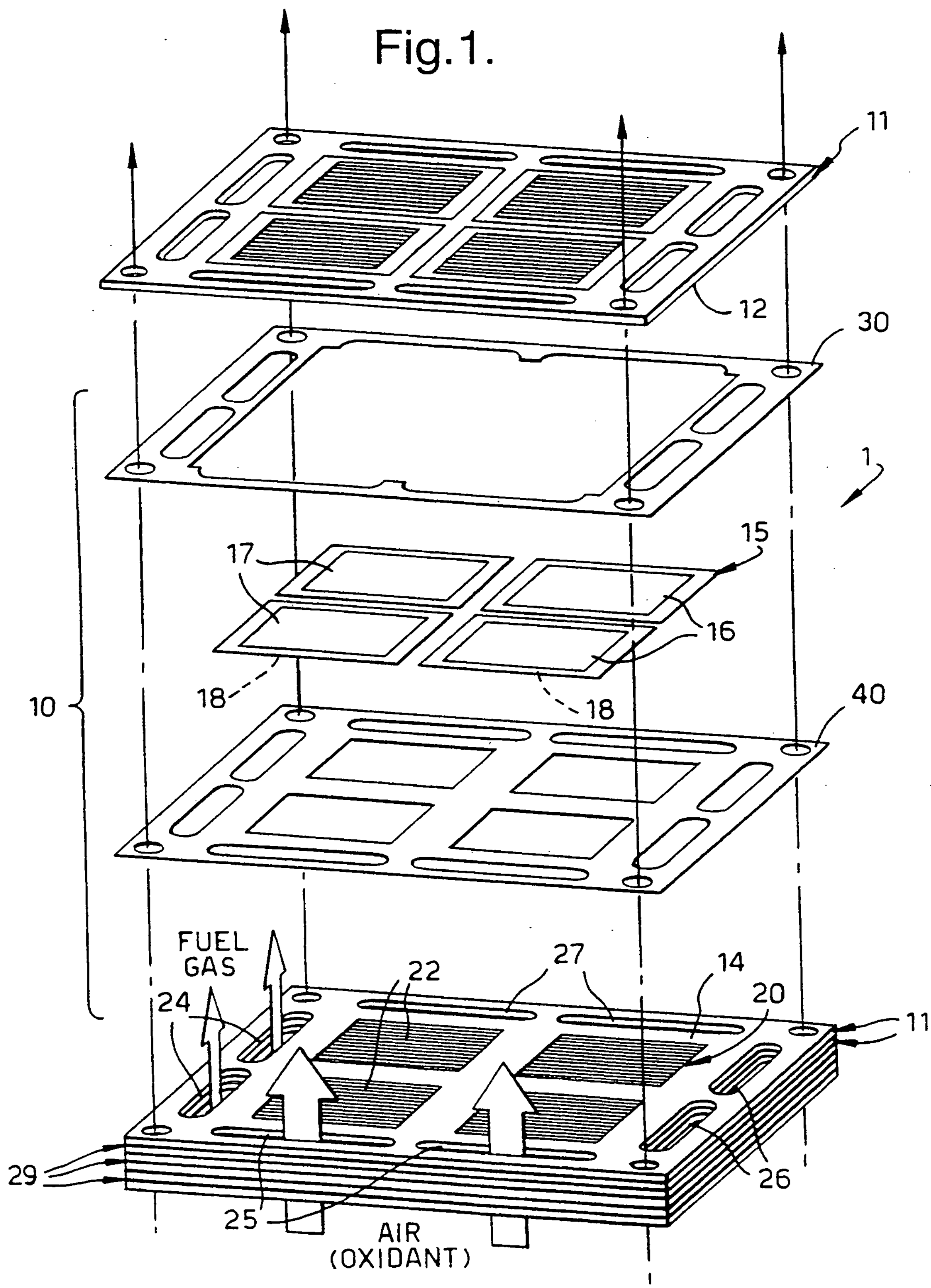
19. A method according to Claim 18, wherein the glass-powder compositions of the bonding layer and of the laminar body are such as to reduce thermal stress between the substrate and laminar body.

20. A method according to Claim 18 or Claim 19 wherein the glass-powder composition of the bonding layer is such when in its glass state prior to crystallisation, it flows and wets the substrate, thereby achieving a strong bond at its interface with the substrate.

21. A method according to any one of claims 14 to 20, with the additional step that a glass layer is applied to the laminar body, said layer of glass having a composition which remains in the glassy viscous state after crystallisation of the laminar body into a glass-ceramic layer.

22. A method of forming a seal between two adjacent separator plates of a fuel cell, said method including a method of forming a glass-ceramic coating according to one of claims 14 to 21.

Fig.1.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(OXIDANT)

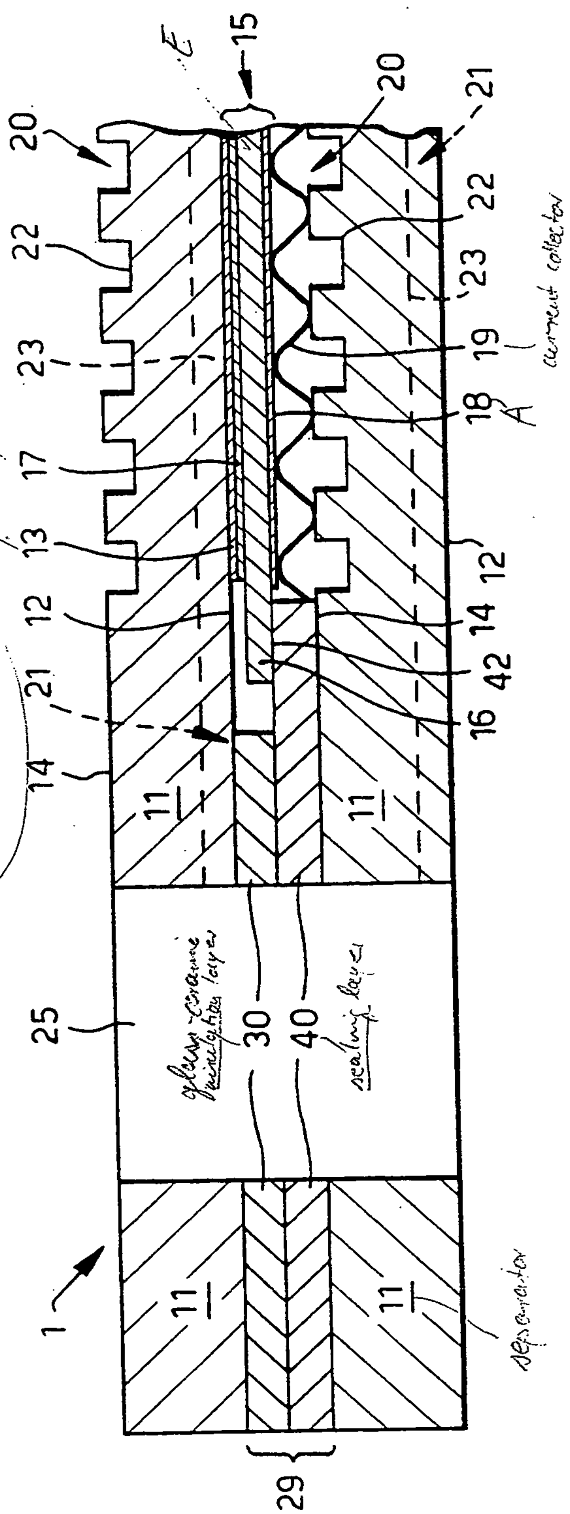
glass-ceramic insulation layer
sealing layer
conductive layer
current collector
separator

Fig.4(a).

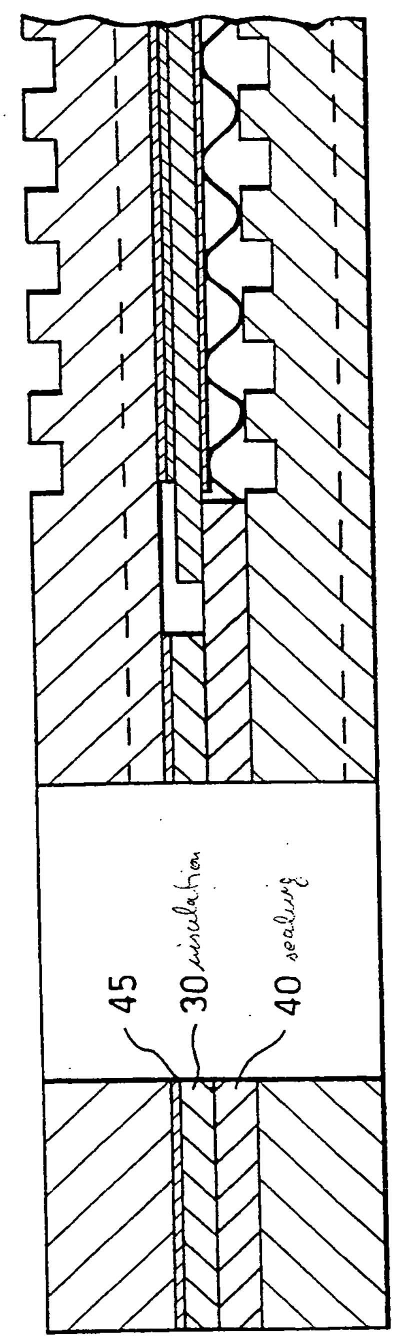
insulation
sealing

Fig.4(b).

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01060

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B18/00 H01M8/02 C04B35/622

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B H01M C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 312 700 A (ISHIDA YOSHIHIKO) 17 May 1994 (1994-05-17) column 5, line 17 - line 33 column 4, line 63 - column 5, line 6; claims 1,2; figures 3,7	1,5,6, 14,28-30
X	DATABASE WPI Section Ch, Week 9707 Derwent Publications Ltd., London, GB; Class J03, AN 97-073034 XP002113706 & JP 08 319181 A (NGK INSULATORS LTD), 3 December 1996 (1996-12-03) abstract	1,5,14, 28

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 August 1999	08/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Andrews, M

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte   .onal Application No
PCT/GB 99/01060

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